

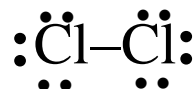
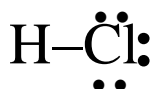
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Lesson-1

I – Molecular Shape: VSEPR Theory

A) Diatomic Molecules:

- The geometry of all diatomic molecules is **linear**.

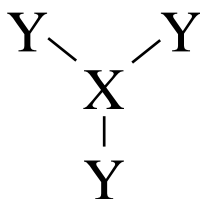


B) VSEPR Models of Polyatomic Molecules:

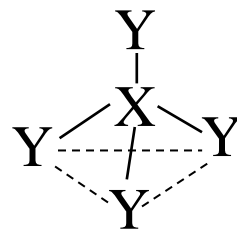
- The valence-shell electron-pair repulsion (VSEPR) model states: *the electron pairs surrounding an atom repel one another and are oriented as far apart as possible.*
- The VSEPR model stipulates that Lewis structures should be written with bonded and non-bonded electron pairs oriented as far apart as possible so as to limit the electron pair repulsions.
- In the VSEPR model, a region about a central atom in which electrons are concentrated is called an **electron domain**.
- An electron domain may consist of a bonded pair of electrons or a non-bonded pair of electrons.
- A double or triple bond is considered to be a single electron domain since all the electrons are concentrated in the same region about the central atom.
- In the VSEPR model, the three-dimensional arrangement of the electron domains about the central atom is called the **electron domain geometry**.
- In the VSEPR model, the three-dimensional arrangement of the atoms in a molecule is called the **molecular geometry**.
- The bonding angles found in a molecule are determined by the **electron domain geometry** of the molecule.



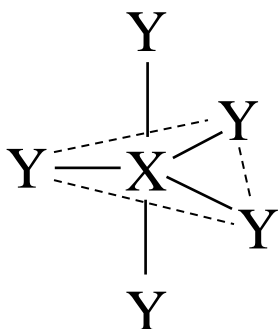
Linear (180°)



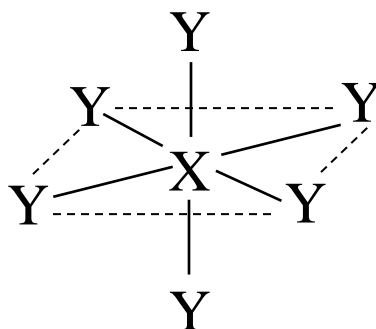
Trigonal planar (120°)



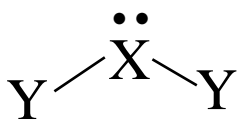
Tetrahedral (109.5°)



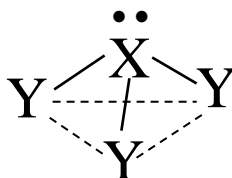
Trigonal bipyramidal (120° & 90°)



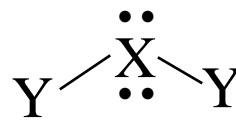
Octahedral (90°)



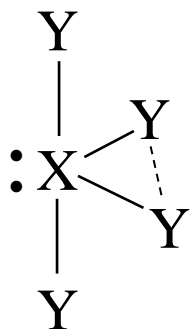
Bent ($< 120^\circ$)



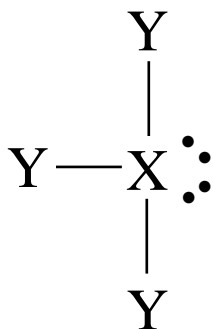
Trigonal pyramidal ($< 109.5^\circ$)



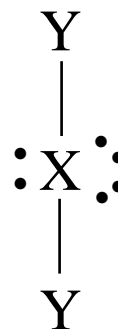
Bent ($< 109.5^\circ$)



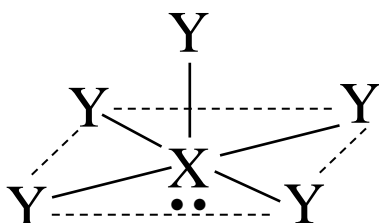
Seesaw (90° & 120°)



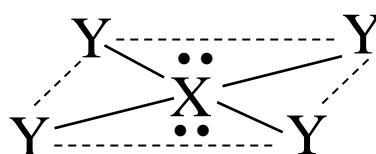
T-shaped (90°)



Linear (180°)



Square pyramidal (90°)



Square planar (90°)

(1) Draw the Lewis structure. (2) State the electron domain geometry. (3) State the molecular geometry. (4) State the bond angle(s) present.

Q1: CO₂

A1:

EDG is _____

MG is _____

Bond angle(s): _____

Q2: CCl₄

A2:

EDG is _____

MG is _____

Bond angle(s): _____

Q3: H₂O

A3:

EDG is _____

MG is _____

Bond angle(s): _____

(1) Draw the Lewis structure. (2) State the electron domain geometry.
(3) State the molecular geometry. (4) State the bond angle(s) present.

Q4: SF_5^{1-}

A4:

EDG is _____

MG is _____

Bond angle(s): _____

Q5: XeF_4

A5:

EDG is _____

MG is _____

Bond angle(s): _____

Q6: BrF_5

A6:

EDG is _____

MG is _____

Bond angle(s): _____

(1) Draw the Lewis structure. (2) State the electron domain geometry.
(3) State the molecular geometry. (4) State the bond angle(s) present.

Q7: Cl_2CO

A7:

EDG is _____

MG is _____

Bond angle(s): _____

Q8: SO_2

A8:

EDG is _____

MG is _____

Bond angle(s): _____

Q9: PH_3

A9:

EDG is _____

MG is _____

Bond angle(s): _____

(1) Draw the Lewis structure. (2) State the electron domain geometry.
(3) State the molecular geometry. (4) State the bond angle(s) present.

Q10: PCl_5

A10:

EDG is _____

MG is _____

Bond angle(s): _____

Q11: ClF_3

A11:

EDG is _____

MG is _____

Bond angle(s): _____

Q12: SF_6

A12:

EDG is _____

MG is _____

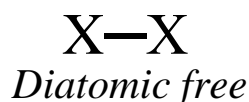
Bond angle(s): _____

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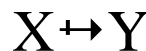
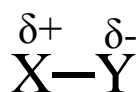
Lesson-2

II – Polarity of Polyatomic Molecules

- Both bond polarity and geometry influence the polarity of molecules of two or more atoms.
- For diatomic molecules, the molecular polarity is entirely due to the bond polarity.

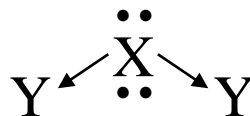
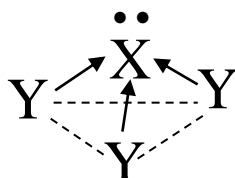
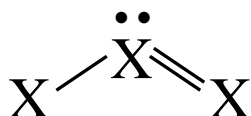
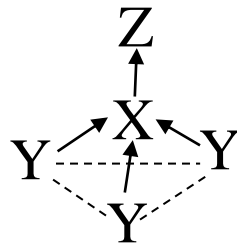
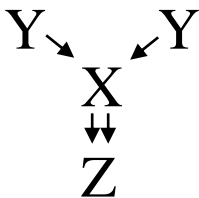
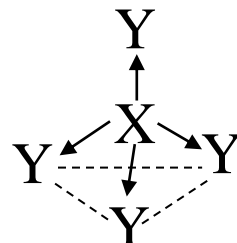
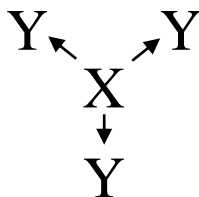


*Diatomic free
elements are
nonpolar molecules.*



*Polar diatomic
molecules can be
symbolized two ways.*

- For polyatomic molecules, the molecular polarity is due to both bond polarity and molecular geometry.



A) Nonpolar Molecules:

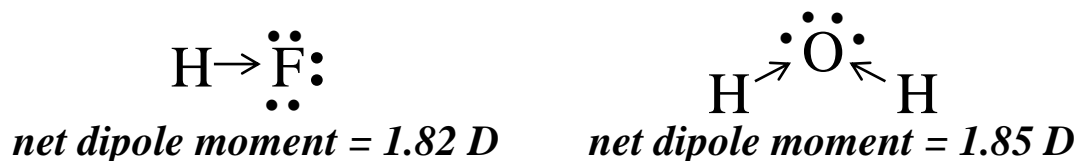
- A **nonpolar molecule** is one with a net balance of charge.



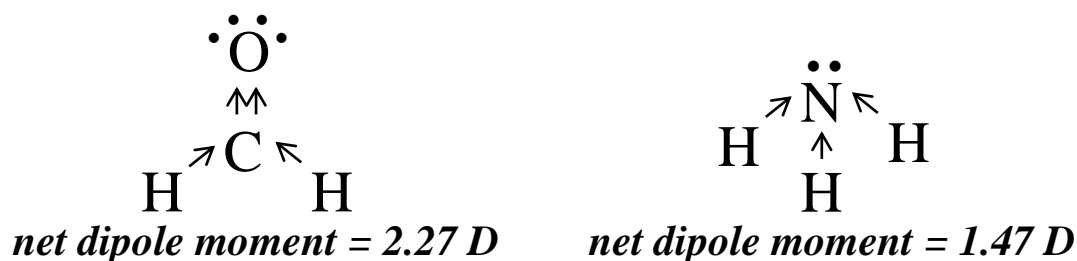
- Nonpolar molecules have a symmetrical geometry.
- Nonpolar molecules are not affected when placed in an electric field.
- Nonpolar molecules have a zero **net dipole moment** (μ).

B) Polar Molecules:

- A **polar molecule** is one without a net balance of charge.



The Debeye (D) is the unit of net dipole moment



- Polar molecules have an asymmetrical geometry.
- Polar molecules are affected when placed in an electric field. They orient themselves so that their partially charged ends point toward the oppositely charged plates.
- Polar molecules have a nonzero **net dipole moment** (μ).

(1) Draw the Lewis structure. (2) State the electron domain geometry. (3) State the molecular geometry. (4) State the bond angles present. (5) State the polarity of the bonds. (6) State the polarity of the molecule. (7) Draw a net dipole moment vector for any molecule with a net dipole moment greater than zero.

Q1: SO₂

A1:

EDG is _____

MG is _____

Bond angle(s): _____

Bond polarity: _____

molecular polarity: _____

Q2: PH₃

A2:

EDG is _____

MG is _____

Bond angle(s): _____

Bond polarity: _____

molecular polarity: _____

Q3: IF₅

A3:

EDG is _____

MG is _____

Bond angle(s): _____

Bond polarity: _____

molecular polarity: _____

(1) Draw the Lewis structure. (2) State the electron domain geometry. (3) State the molecular geometry. (4) State the bond angles present. (5) State the polarity of the bonds. (6) State the polarity of the molecule. (7) Draw a net dipole moment vector for any molecule with a net dipole moment greater than zero.

Q4: XeF₄

A4:

EDG is _____

MG is _____

Bond angle(s): _____

Bond polarity: _____

molecular polarity: _____

Q5: BCl₃

A5:

EDG is _____

MG is _____

Bond angle(s): _____

Bond polarity: _____

molecular polarity: _____

Q6: SF₄

A6:

EDG is _____

MG is _____

Bond angle(s): _____

Bond polarity: _____

molecular polarity: _____

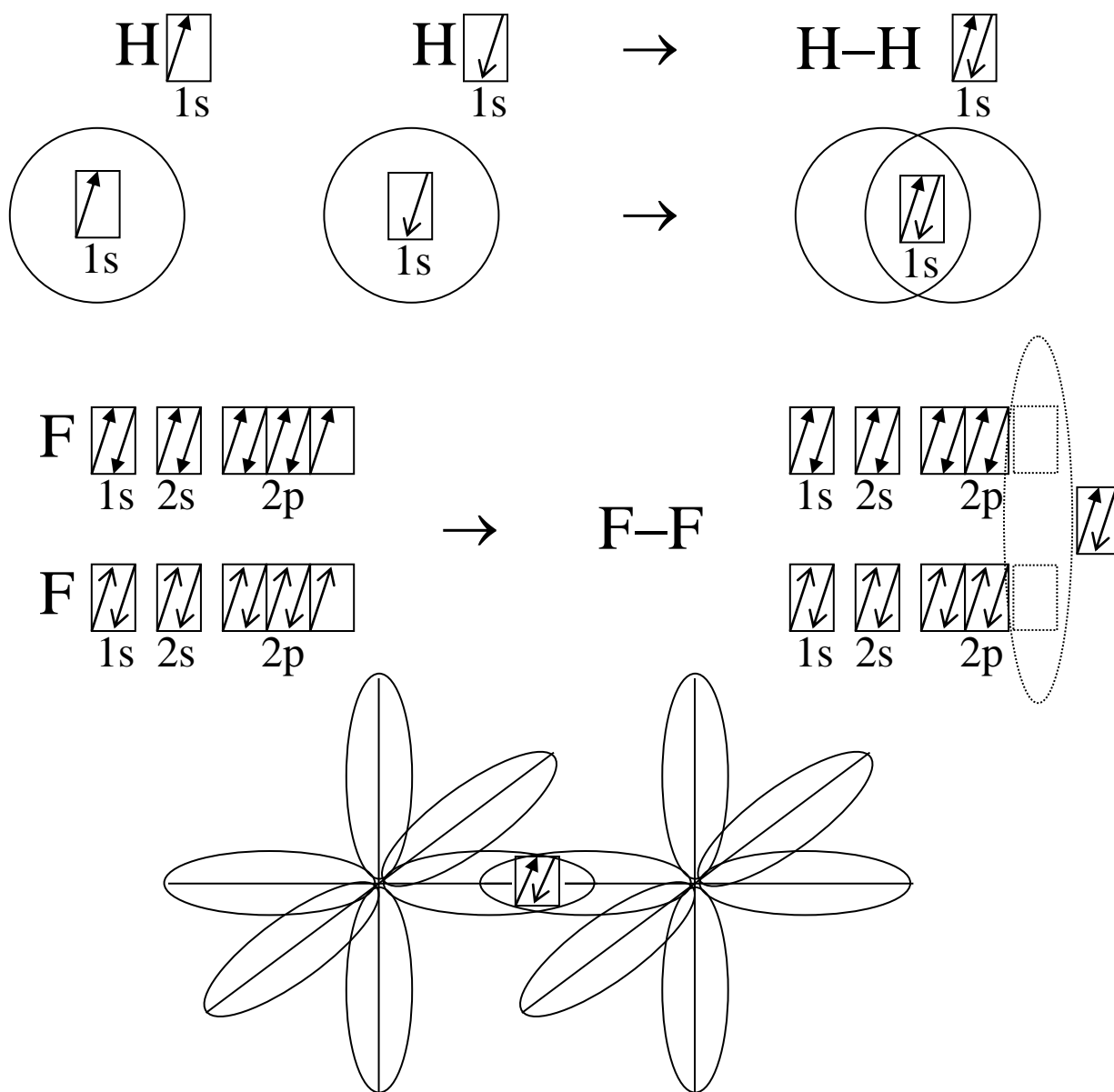
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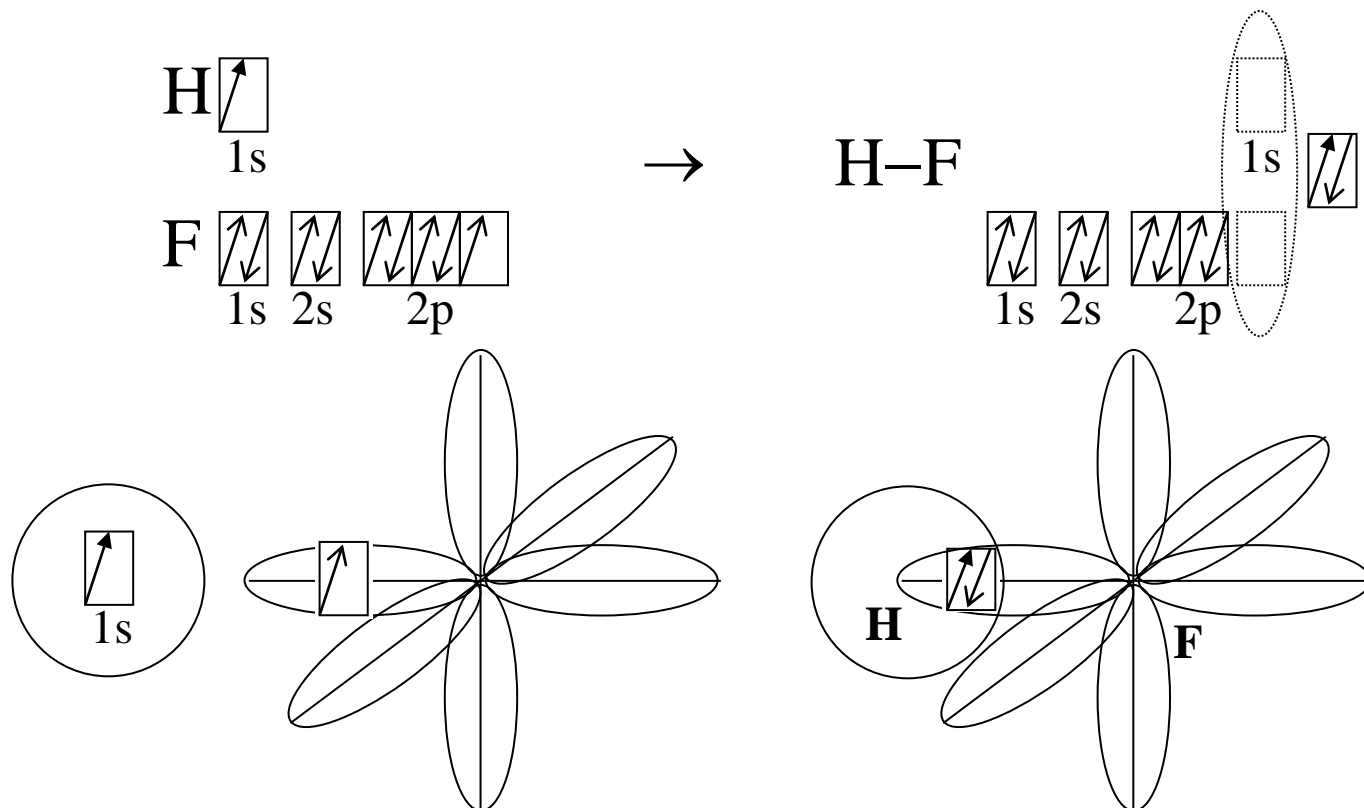
Lesson-3

III – Valence Bond (VB) Theory

- Lewis Models and VSEPR theory tell us nothing about the orbitals in which the bonding electrons are found or about the energies that these electrons have in the molecules.
- According to **valence bond theory**, a covalent bond forms when the orbitals of two atoms overlap and are occupied by a pair of electrons of opposite spin.

A) Covalent Bonding and Orbital Overlap:



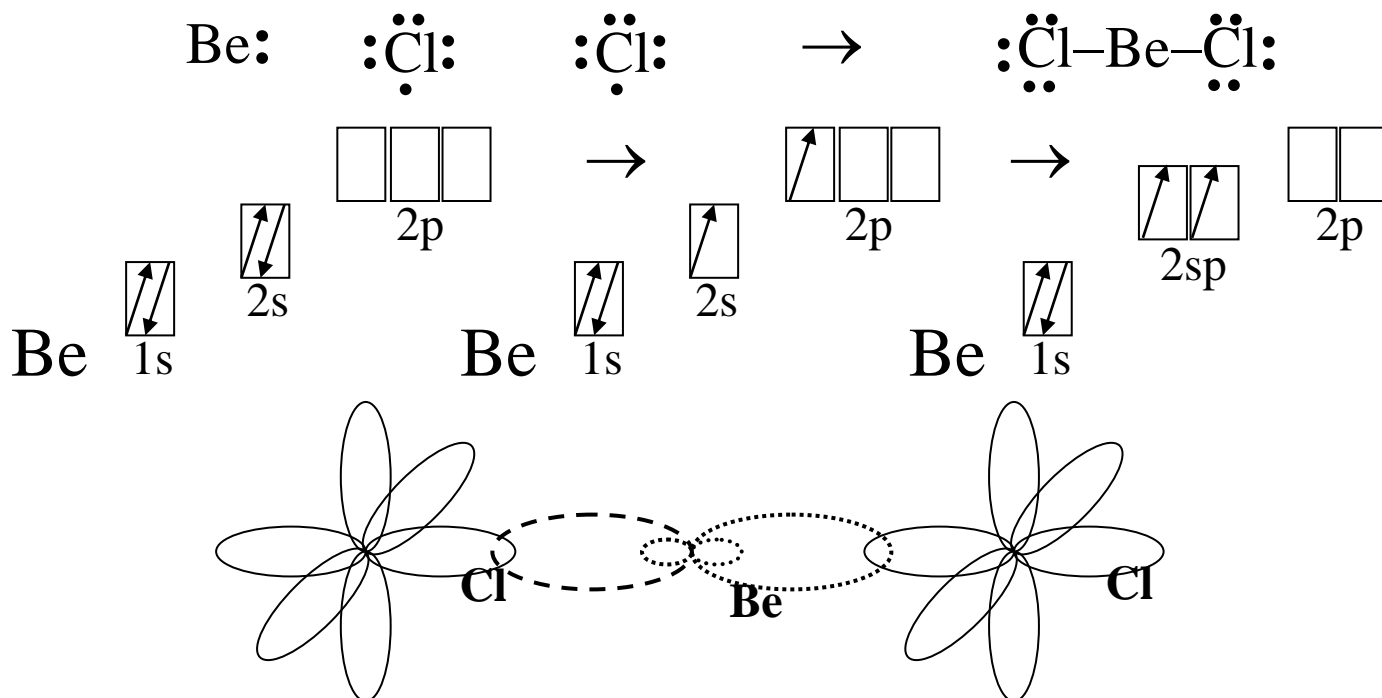


- In most molecules, the orbitals occupied by electron pairs are seldom "pure" **s** or **p** orbitals. Instead they are "hybrid" orbitals, formed by combining **s** and **p** or **s**, **p** and **d** orbitals.

B) VB Theory and Simple Hybrid Orbitals:

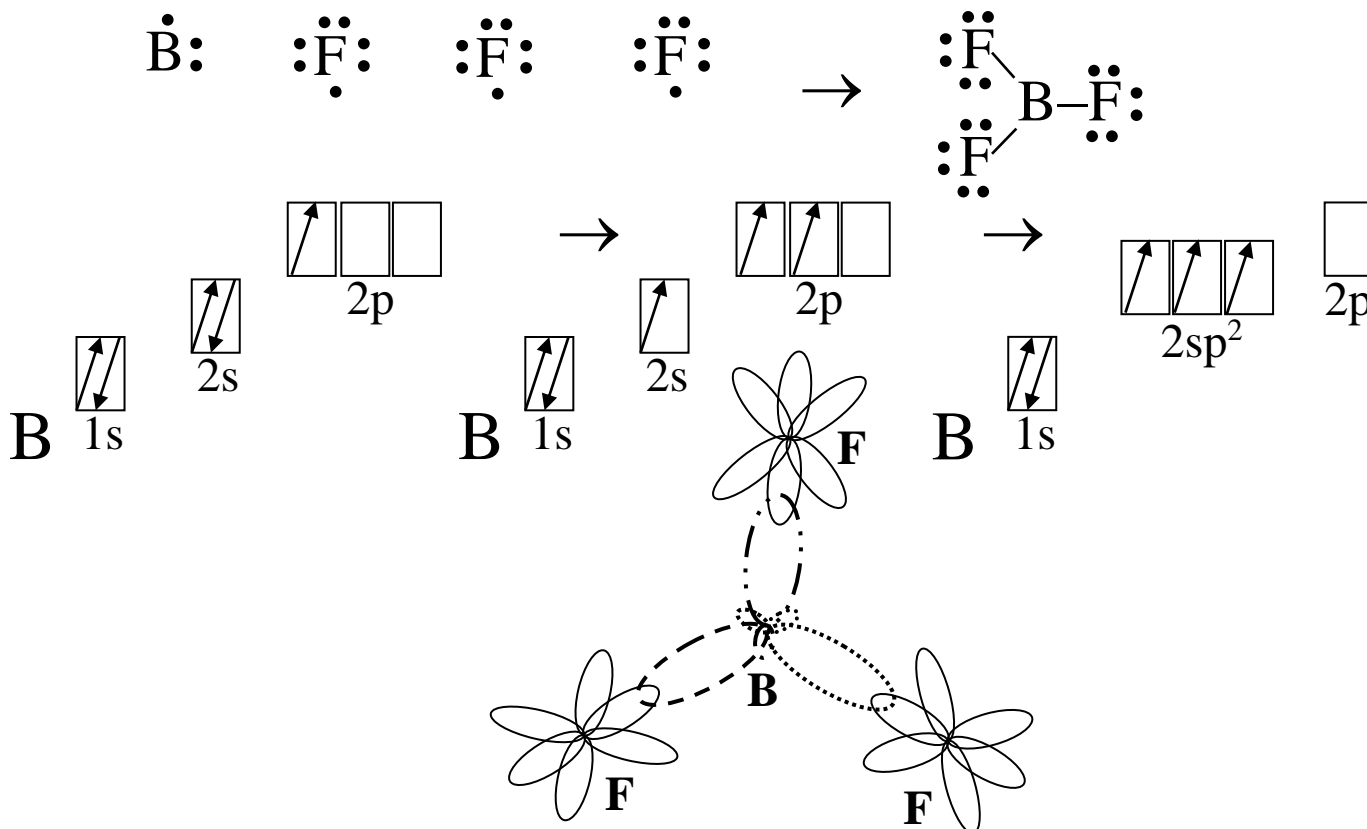
- **sp hybridization** [2 electron pairs around the central atom]

According to the valence bond (VB) theory, how does beryllium form two equal covalent bonds with chlorine?



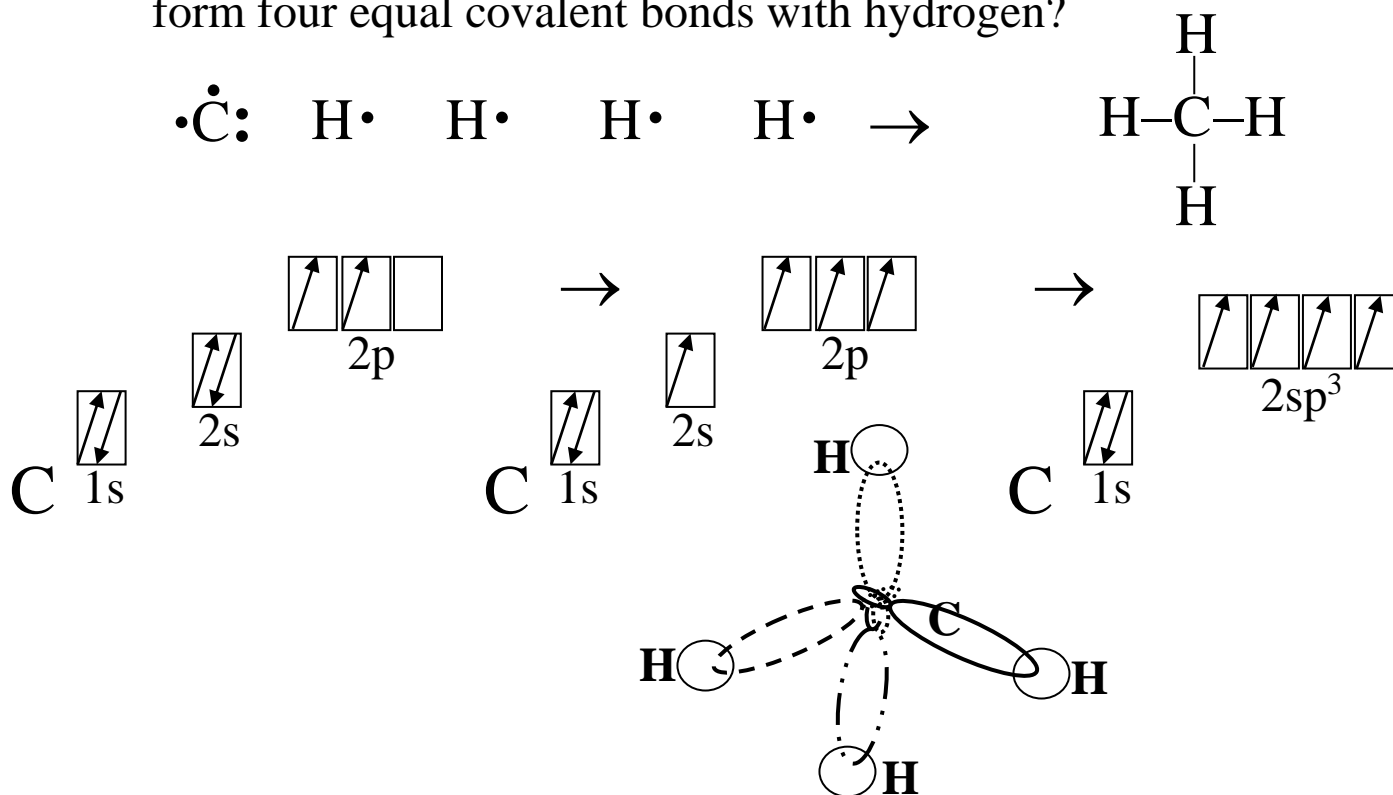
- **sp² hybridization** [3 electron pairs around the central atom]

According to the valence bond (VB) theory, how does boron form three equal covalent bonds with fluorine?



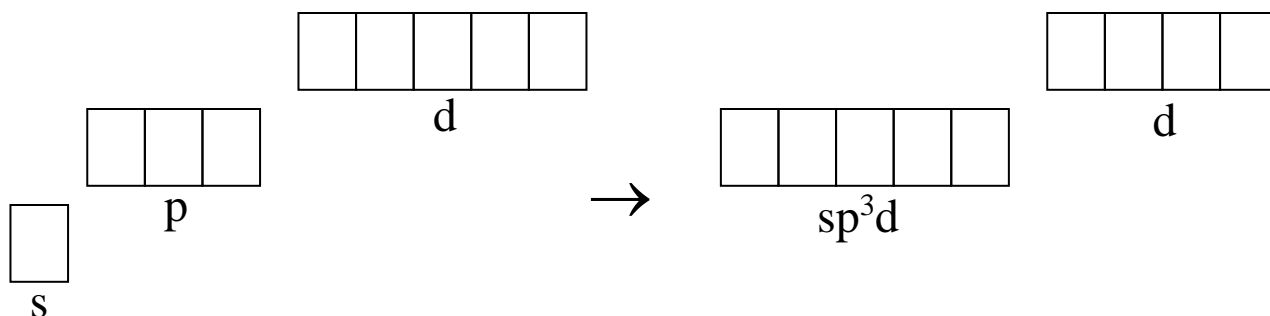
- **sp³ hybridization** [4 electron pairs around the central atom]

According to the valence bond (VB) theory, how does carbon form four equal covalent bonds with hydrogen?

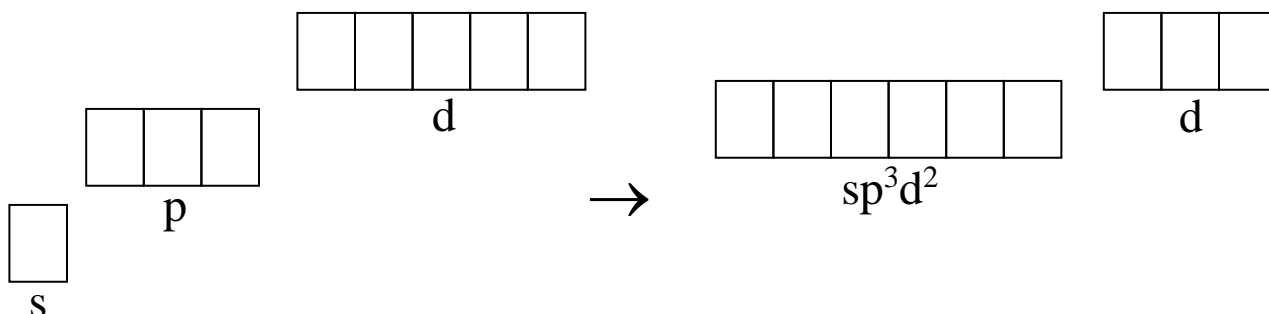


C) VB Theory and Expanded Hybrid Orbitals:

- sp^3d hybridization [5 electron pairs around the central atom]

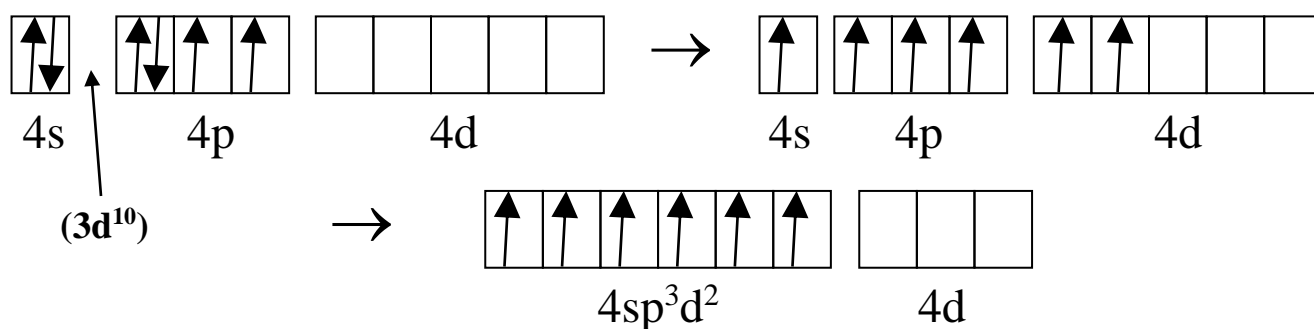


- sp^3d^2 hybridization [6 electron pairs around the central atom]



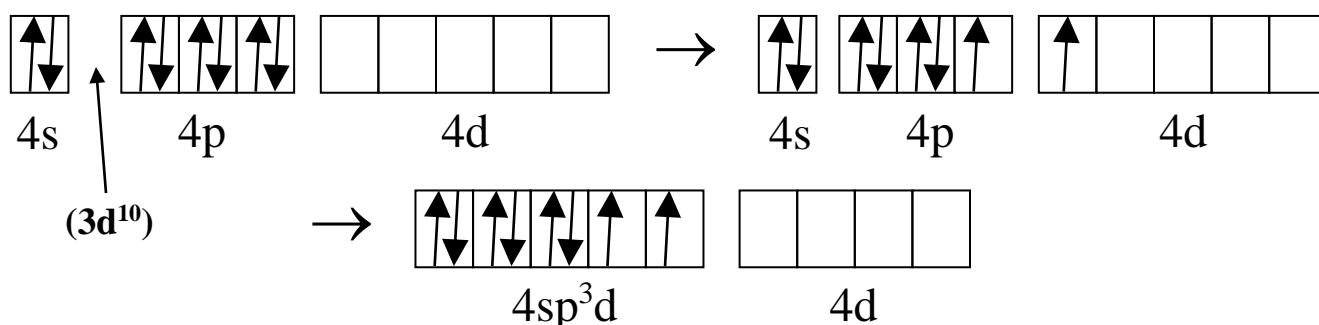
Q1: Draw the valence orbital model for a selenium atom and for the selenium atom in SeF_6 .

A1: In SeF_6 , selenium undergoes sp^3d^2 hybridization.



Q2: Draw the valence orbital model for a krypton atom and for the krypton atom in KrF_2 .

A2: In KrF_2 , krypton undergoes sp^3d hybridization.

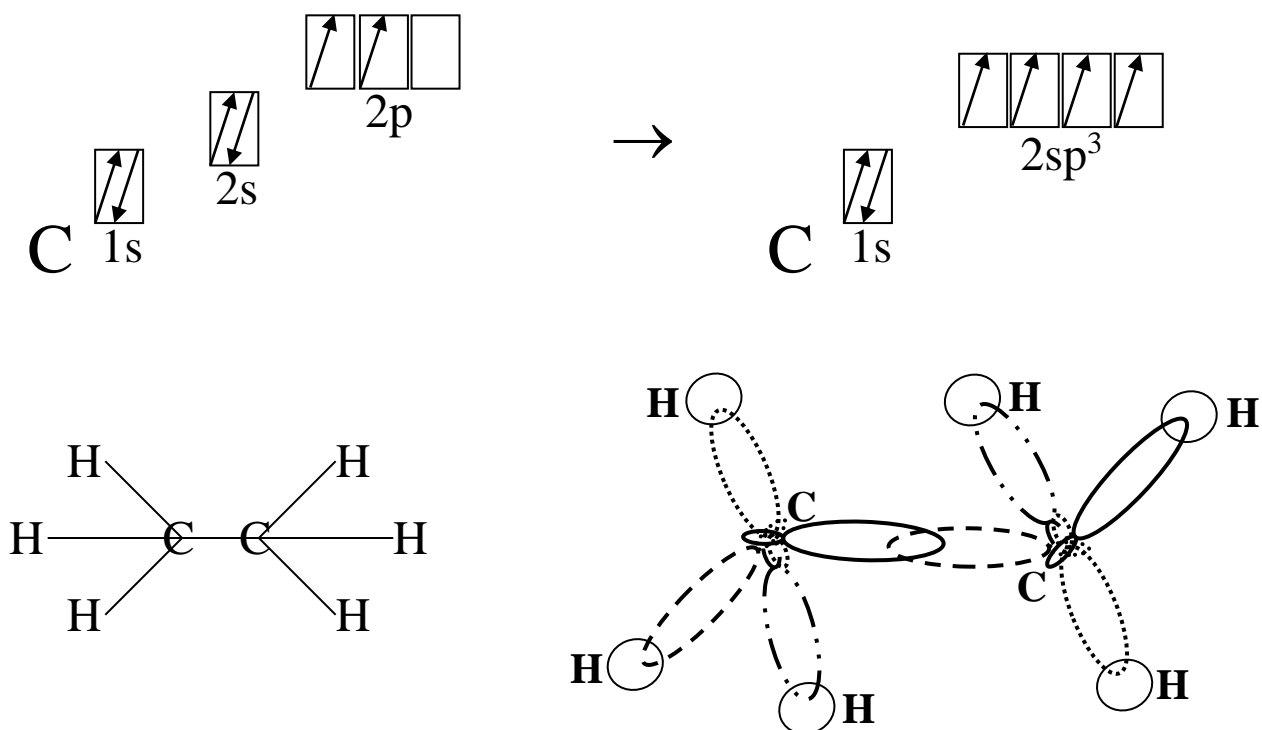


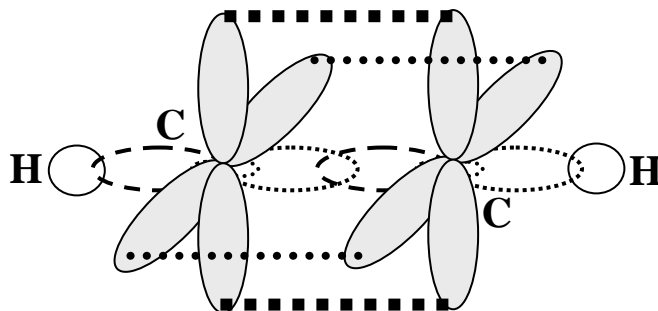
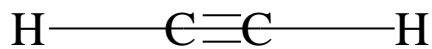
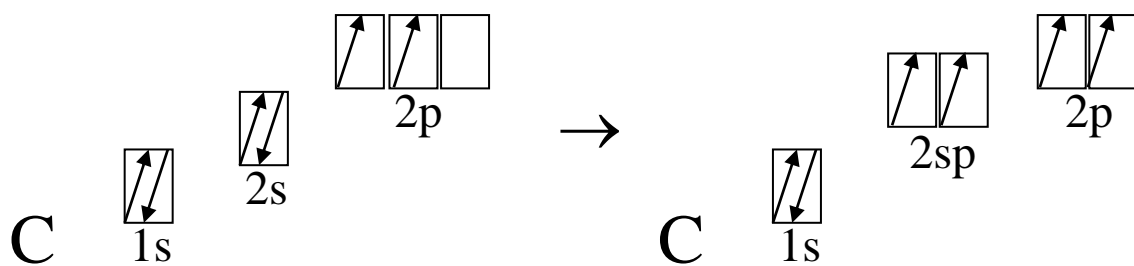
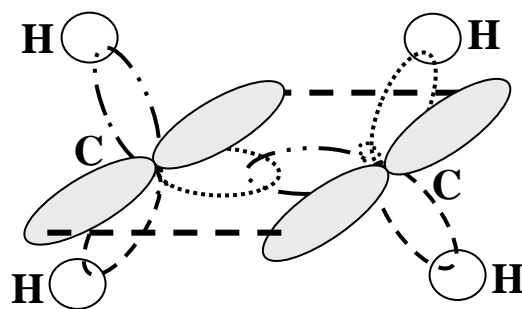
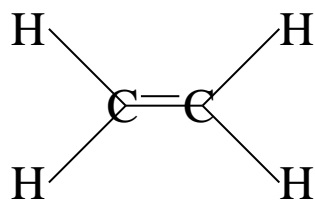
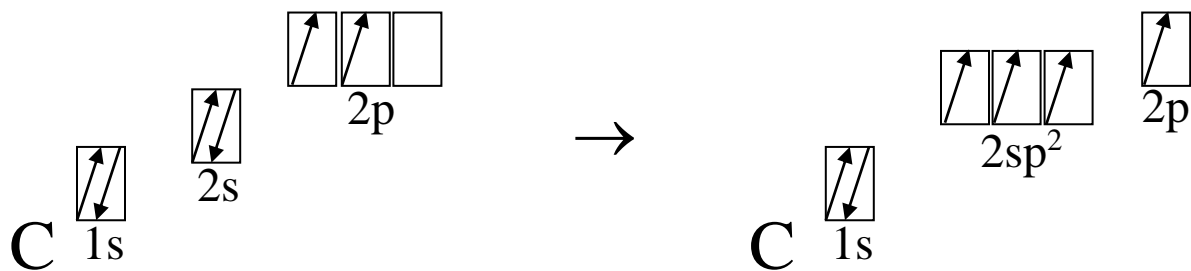
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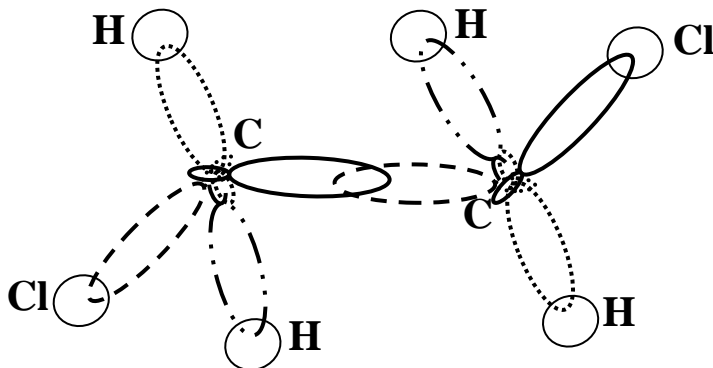
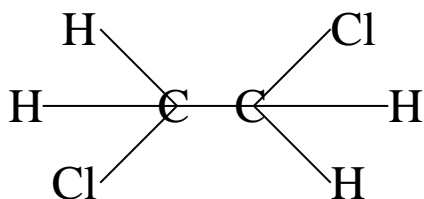
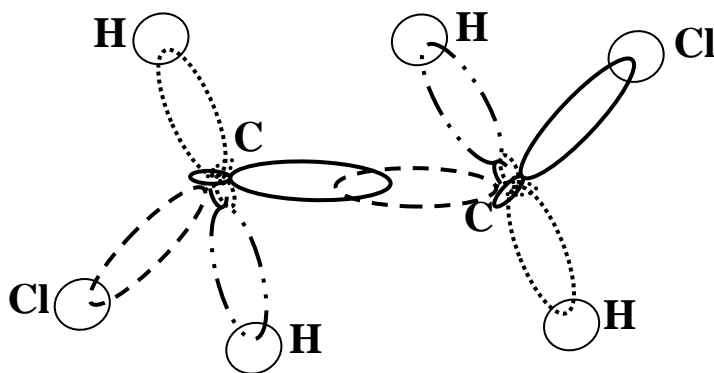
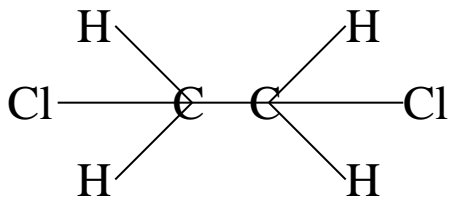
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VI – Multiple Bonds and the Valence Bond Theory

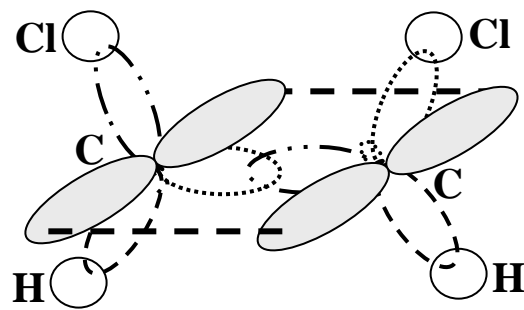
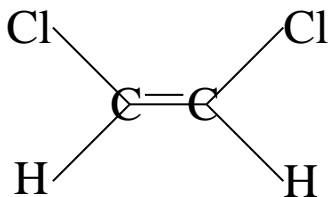
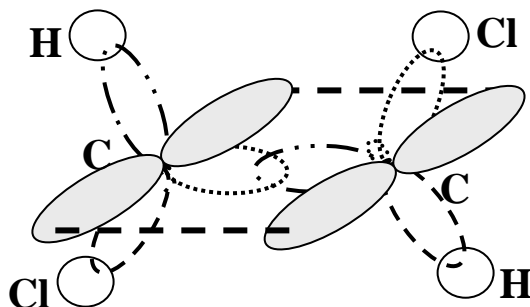
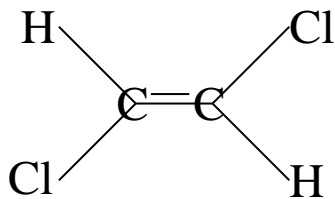
- According to the VB model, a covalent bond forms when the orbitals of two atoms overlap and are occupied by a pair of electrons of opposite spin.
- When the orbitals overlap along the same axis as the two nuclei of the bonding atoms, the bond is called a **sigma (σ) bond**. All single bonds are sigma bonds.
- When the orbitals overlap perpendicularly to the axis of the two nuclei of the bonding atoms, the bond is called a **pi (π) bond**.
- A **double bond** consists of one sigma bond and one pi bond. A **triple bond** consists of one sigma bond and two pi bonds.
- According to the VB model, hybridization only occurs in orbitals that form sigma bonds. ***Orbitals that form pi bonds ARE NOT hybridized.***







- The two structures of $\text{C}_2\text{H}_4\text{Cl}_2$ are the same. The single bond between the carbon atoms acts like an axel that can spin.



- The two structures of $\text{C}_2\text{H}_2\text{Cl}_2$ are different. The double bond between the carbon atoms is rigid and can NOT spin.
- These two structures are called **geometric isomers**.

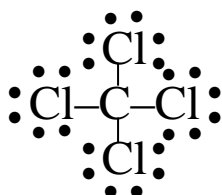
- Q1:** (a) What is the difference between a localized π bond and a delocalized π bond?
- (b) How can you determine whether a molecule or ion will exhibit delocalized π bonding?
- (c) Is the π bond in NO_2^{1-} localized or delocalized?

- A1:** (a) In a localized π bond the electron density is concentrated between the two atoms forming the bond. In a delocalized π bond the electron density is spread over all of the atoms that contribute p orbitals to the network.
- (b) The existence of more than one resonance form is a good indication that a molecule or ion will exhibit delocalized π bonding.
- (c) Since the NO_2^{1-} ion exhibits resonance then the π bond in NO_2^{1-} will be delocalized.

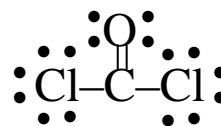


- Q2:** (a) Draw the Lewis structures for (i) CCl_4 and (ii) CCl_2O .
- (b) What is the hybridization at the carbon atom in each?
- (c) The carbon atom in CCl_4 cannot participate in multiple bonding whereas the carbon atom in CCl_2O can. Explain this observation in terms of the carbon's hybridization.

A2: (a) (i)



(ii)



(b) (i) sp^3 hybridization

(ii) sp^2 hybridization

- (c) Since the carbon atom in CCl_4 is sp^3 hybridized there are no unhybridized p-orbitals available for the π overlap that is needed for multiple bonds. The carbon atom in CCl_2O is sp^2 hybridized, with one unhybridized p-orbital available to form the π overlap necessary for the $\text{C}=\text{O}$ double bond.

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Lesson-5

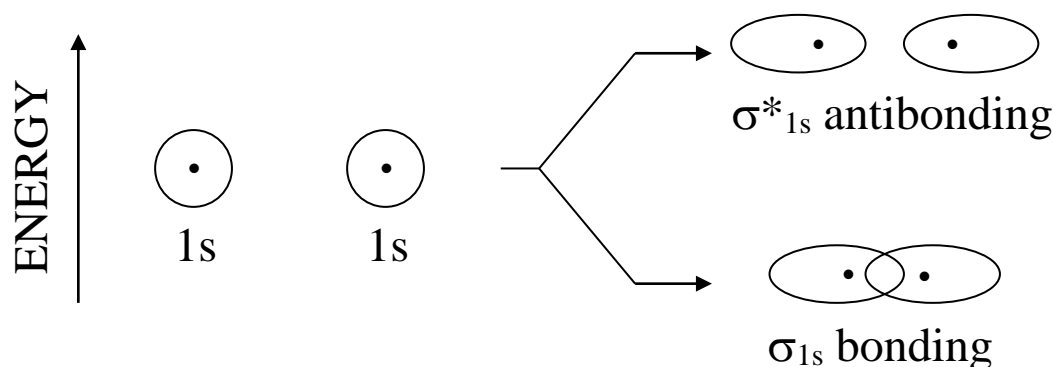
V – Molecular Orbitals

- **VSEPR theory** and **VB theory** helps to explain molecular geometry (shape). The two models compliment each other.
- Also, in both models, the atoms in a molecule are bonded by electrons that are localized between two (or a few) atoms.
- **VB theory** (which is based on quantum mechanics) also explains orbital energies as well as sigma (σ) and pi (π) bonding.
- However, neither model can explain the magnetic or spectral properties of molecules. ***Oxygen (O_2) is paramagnetic and neither model would predict this!***
- **Molecular Orbital (MO) theory** (which is based on quantum mechanics) explains the bonding of atoms in a molecule in terms of nuclei held together by electron orbitals that are delocalized over the entire molecule.
- In **MO theory**, the orbitals belong to the entire molecule. As with atomic orbitals (AOs), **MOs** have a given energy and shape.

A) Formation of Molecular Orbitals:

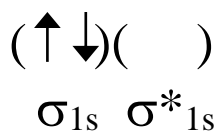
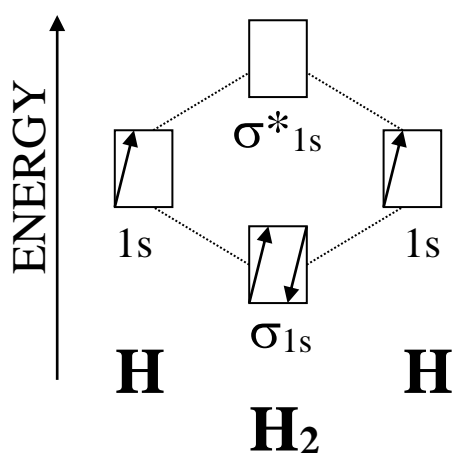
- In a molecule, the molecular orbitals (**MOs**) are formed by the combination of the atoms' atomic orbitals (AOs). The number of MOs formed is always equal to the number of AOs combined.
- MOs are arranged in order of increasing energy.
- Electrons are distributed among the available **MOs** according to the following rules:
 - Each **MO** only holds two electrons with opposite spins.
(**Pauli exclusion principle**)
 - Electrons occupy the lowest (in energy) available **MO**.
(**aufbau principle**)
 - **MO** of equal energy are half-filled before any is filled.
(**Hund's Rule**)

- All **MOs** come in pairs. One is called the **bonding MO** (a region of high electron density between the nuclei) and the other is called the **antibonding MO** (a region which includes zero electron density between the nuclei). ***The bonding MO always has lower energy than the antibonding MO.***
- Only AO's of similar energy and orientation will combine to form the bonding and antibonding **MOs**.

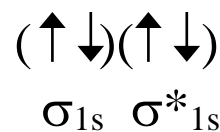
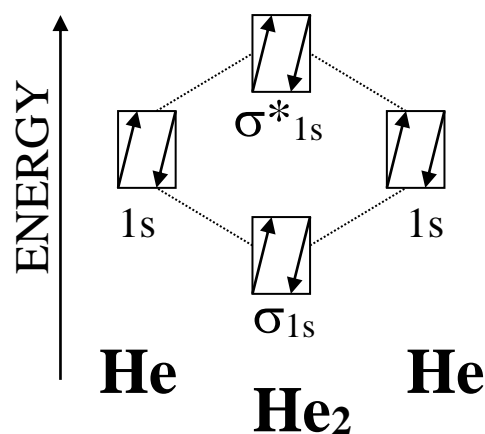


- The bond order between bonded atoms is determined as follows:
Bond Order = $\frac{\# \text{Bonding Electrons} - \# \text{Antibonding Electrons}}{2}$
- The higher the bond order is, the stronger the bond will be.
- If the bond order is zero then no bond exists!

B) Homonuclear Diatomic Molecules of Period-1:

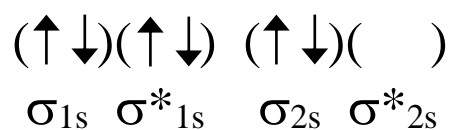
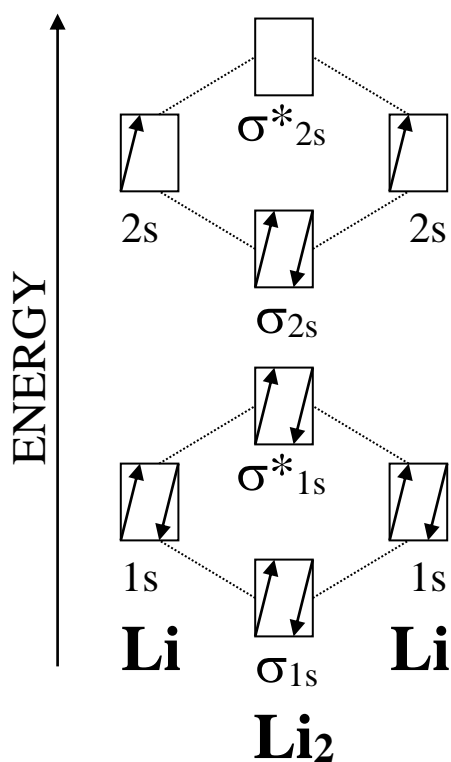


Bond order = 1

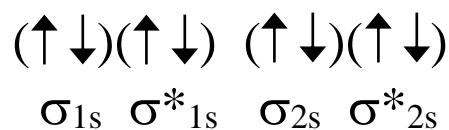
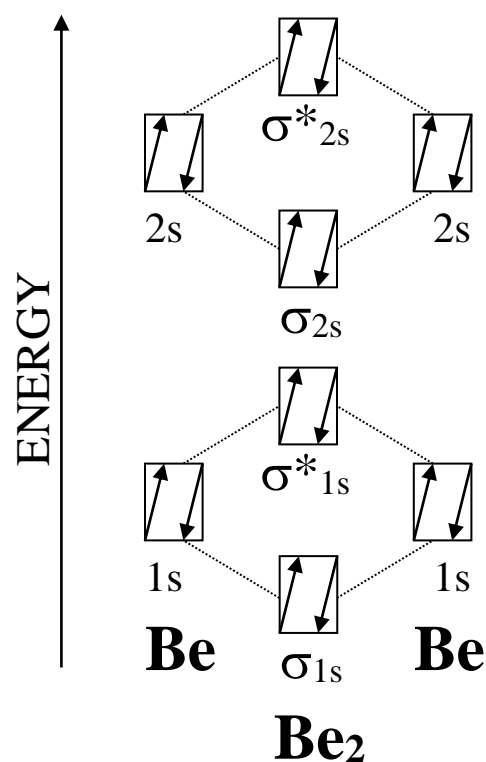


Bond order = 0

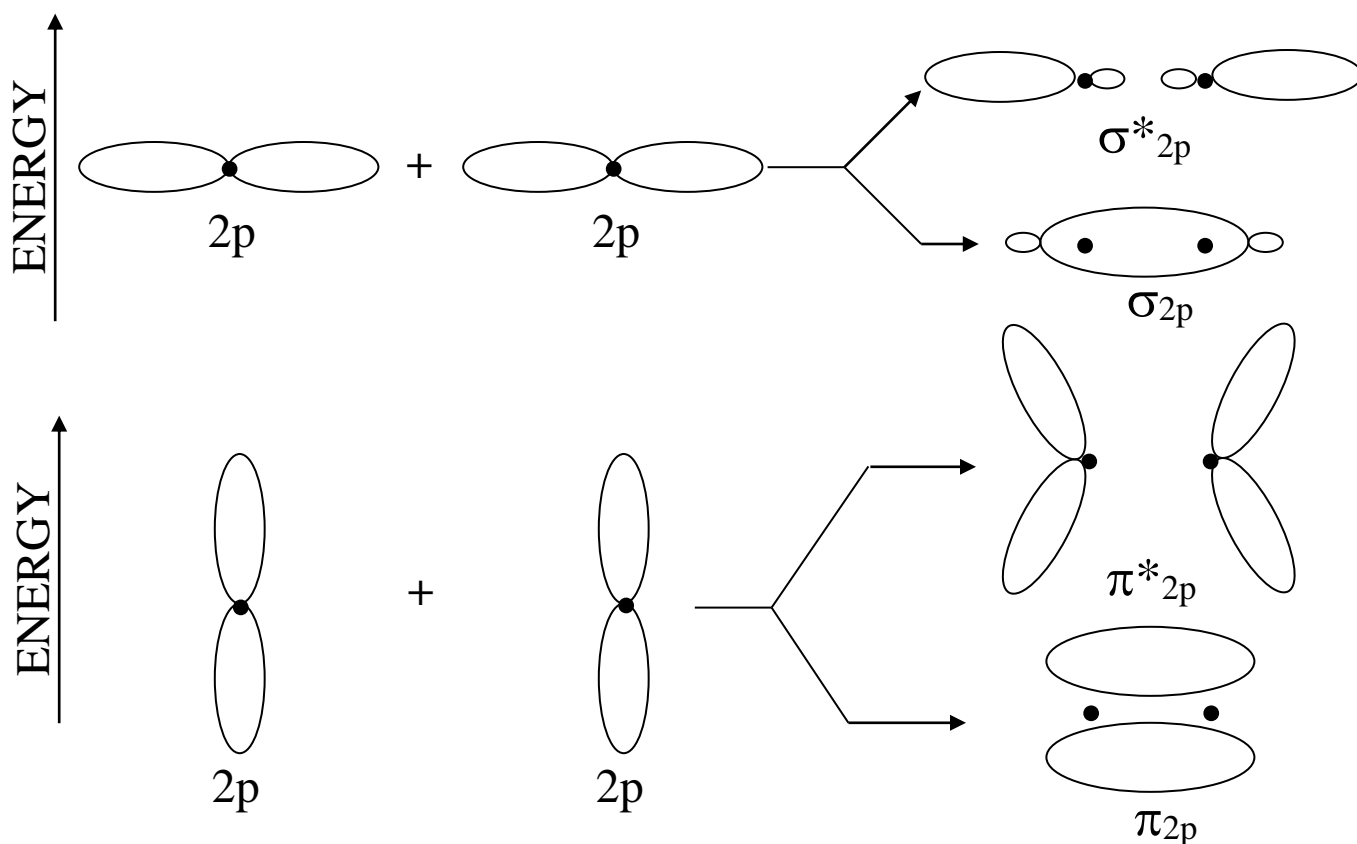
C) Homonuclear Diatomic Molecules of Period-2:



Bond order = 1



Bond order = 0



Q1: Determine the MO orbital configurations for (i) CN^{1+} , (ii) CN , and (iii) CN^{1-} [assume the MO ordering is that of C_2 and N_2].

A1: (i) CN^{1+} : $(\uparrow\downarrow)(\uparrow\downarrow)(\uparrow\downarrow)(\uparrow\downarrow)(\quad)(\quad)(\quad)(\quad)$
 $\sigma_{2s} \quad \sigma_{2s}^* \quad \pi_{2p} \quad \pi_{2p} \quad \sigma_{2p} \quad \pi_{2p}^* \quad \pi_{2p}^* \quad \sigma_{2p}^*$

(ii) CN : $(\uparrow\downarrow)(\uparrow\downarrow)(\uparrow\downarrow)(\uparrow\downarrow)(\uparrow)(\quad)(\quad)(\quad)$
 $\sigma_{2s} \quad \sigma_{2s}^* \quad \pi_{2p} \quad \pi_{2p} \quad \sigma_{2p} \quad \pi_{2p}^* \quad \pi_{2p}^* \quad \sigma_{2p}^*$

(iii) CN^{1-} : $(\uparrow\downarrow)(\uparrow\downarrow)(\uparrow\downarrow)(\uparrow\downarrow)(\uparrow\downarrow)(\quad)(\quad)(\quad)$
 $\sigma_{2s} \quad \sigma_{2s}^* \quad \pi_{2p} \quad \pi_{2p} \quad \sigma_{2p} \quad \pi_{2p}^* \quad \pi_{2p}^* \quad \sigma_{2p}^*$

Q2: Calculate the bond order for (i) CN^{1+} , (ii) CN , and (iii) CN^{1-} .

A2: (i) $\text{BO} = 2.0$
(ii) $\text{BO} = 2.5$
(iii) $\text{BO} = 3.0$

Q3: For (i) CN^{1+} , (ii) CN , and (iii) CN^{1-} , indicate which one(s) are paramagnetic and which one(s) are diamagnetic

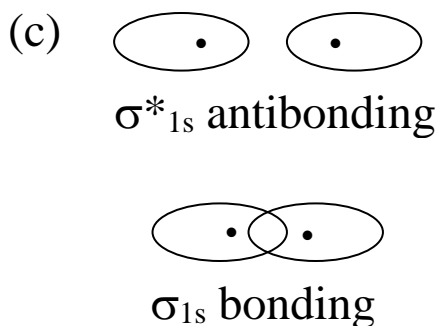
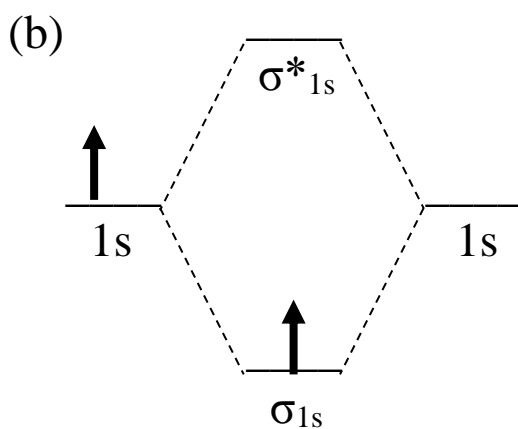
A3: (i) diamagnetic
(ii) paramagnetic
(iii) diamagnetic

Q4: For (i) CN^{1+} , (ii) CN , and (iii) CN^{1-} , write the valence electron configuration of the molecule or ion in terms of its MO's.

A4: (i) $\sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4$
(ii) $\sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4 \sigma_{2p}^1$
(iii) $\sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4 \sigma_{2p}^2$

Q5: Consider the H_2^{1+} ion. (a) How many electrons are there in the ion? (b) Draw the energy-level diagram of the ion. (c) Sketch the molecular orbitals of the ion. (d) Write the electron configuration of the ion in terms of its MO's. (e) What is the bond order of the ion? (f) Suppose that the ion is excited by light so that an electron moves from a lower-energy MO to a higher-energy MO. Would you expect the excited-state ion to be stable or to fall apart? Explain.

A5: (a) There is one electron.



(d) σ_{1s}^1

(e) $\text{BO} = \frac{1}{2}$

(f) Fall apart. If the lone electron in the ion is excited to the σ^*_{1s} antibonding MO, its energy would be higher than the energies of the $1s$ atomic orbitals. Thus the H_2^{1+} ion would decompose into a hydrogen atom (H) and a hydrogen ion (H^{1+}).